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# Cu rich domains and secondary phase in PVD-CdS / PVD-CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> heterojunctions

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**Abstract** — The Cu migration behavior in PVD-CdS/PVD-Cu(In,Ga)Se<sub>2</sub> (CIGS) is investigated by high resolution electron microscopy and energy dispersive X-ray spectroscopy (EDS) mapping techniques based on scanning transmission electron microscopy (STEM). The incorporation of Cu into CdS forms Cu-rich domains of uniform coverage on the CIGS surface and has no effect on epitaxy of the CdS film. In some cases Cd is completely depleted and replaced by Cu, resulting in a Cu-S binary compound epitaxially grown on the CIGS, which is most likely to be cubic Cu<sub>2</sub>S by lattice spacing measurement from HREM images and EDS element quantification. The presence of a binary Cu-S phase as a heterojunction partner material may have significant impact on the resulting device performance although only modest loss of  $V_{oc}$  occurs in the devices studied.

**Index Terms** — Cu(In,Ga)Se<sub>2</sub> photovoltaics, CdS Structure, transmission electron microscopy, STEM-EDS mapping

## I. INTRODUCTION

Thin film solar cells based on Cu(In,Ga)Se<sub>2</sub> (CIGS) absorbers have gained wide attention for several decades due to their steady increase in solar conversion efficiency[1]. Normally, a thin n-type CdS buffer layer is deposited to protect the CIGS surface from sputtering damage by subsequent ZnO deposition and to form a *p-n* heterojunction with the *p* type CIGS. So far chemical bath deposited (CBD) CdS is widely adopted as a standard material to produce high efficiency CdS/CIGS solar cells. The main drawback associated with the CBD process is its non-compatibility with the other vacuum based film deposition procedure. From the viewpoint of large scale manufacturability, non-vacuum break method, such as physical vapor deposition (PVD), should be more desirable given that PVD-CdS/CIGS can deliver competitive efficiency compared to its CBD counterpart. Unfortunately, it has been a common recognition for many years that PVD-CdS/CIGS solar cells exhibited inferior efficiency. Recently a PVD-CdS/CIGS solar cell demonstrated 15.7% efficiency[1] under the global AM1.5 spectrum (1000 W/m<sup>2</sup>) with an aperture area of 9703 cm<sup>2</sup>. Thus, understanding the structural and chemical characteristics of the PVD-

CdS/CIGS heterojunction is important and critical for further optimization of the device performance. Previous work[2] from our group suggested that large domains (several hundreds of nms or sometimes in  $\mu$ m) of cubic (zinc-blende, zb) and hexagonal (wurtzite, wz) CdS epitaxially grown on CIGS surface coexist in the PVD materials. In addition, preliminary scanning transmission electron microscopy (STEM)-energy dispersive X-ray spectroscopy (EDS) line profiles across the heterojunction revealed Cu migration from the CIGS into the CdS up to 20 nm from the hetero-interface. This indicates that, like CBD-CdS[3-5], there is significant elemental intermixing across the PVD-CdS/CIGS heterojunction.

In this work, using STEM-EDS spectrum imaging, we were able to obtain elemental maps with high signal-to-noise ratio and show that, similar to CBD-CdS, there are Cu rich layers in the CdS as well as Cd doping on CIGS surface. This is in contrast with report by Abou-Ras *et al.*[6] that showed no Cd doping of CIGS in a PVD-CdS/CIGS heterojunction. The Cu rich domains show complete epitaxy on the CIGS. Furthermore, we find local domains of pure cubic Cu<sub>2</sub>S, epitaxially grown on the CIGS surface.

## II. EXPERIMENT

All layers that comprise MiaSolé's solar cell are deposited sequentially onto a flexible stainless steel substrate in a single pass in an all-PVD process system. One difference of this approach compared to most other manufacturing methods is the replacement of the chemical bath deposited CdS layer with a PVD CdS deposition. All of the transmission electron microscopy (TEM) samples were prepared by a lift-out method on a FEI Helios Nanolab 600i focused ion beam (FIB) instrument. Finally all TEM samples were put into a Fischione Model 1040 NanoMill specimen preparation system for target milling to further minimize the Ga-induced amorphous layer and damage from the FIB. The STEM-EDS maps were obtained in a Titan-X chemi-STEM microscope (National

Center for Electron Microscopy, Lawrence Berkeley National Lab), which is equipped with a Super-X detector; enabling elemental mapping with high signal/noise ratio, typically in several minutes. The K lines of all the elements were utilized for the EDS maps and quantification. Before acquiring EDS maps, the heterojunctions were oriented to a CIGS [021] zone axis where clear high resolution TEM images of the hetero-interface could be recorded without any indication of overlap between the CIGS grains and the CdS layers to ensure the interface is parallel to the electron beam.

### III. RESULTS

Fig. 1 displays a representative HREM image of the zb CdS phase on the CIGS surface. It can be seen that the interface is coherent and no notable defects were observed in the CdS other than stacking faults along (111) planes. The epitaxial relationship is  $\{111\}_{\text{CdS}} \parallel \{112\}_{\text{CIGS}}$ ,  $(001)_{\text{CdS}} \parallel (200)_{\text{CIGS}}$  and  $[110]_{\text{CdS}} \parallel [021]_{\text{CIGS}}$ . More details can be found in Ref. 2. STEM maps acquired in this region are shown in Fig. 2. The most apparent feature is the uniform Cu rich layer on the CIGS surface over the observed region. Combining with Fig. 1, we find that the Cu enrichment roughly occurs in the region where stacking faults are found, suggesting that incorporation of Cu may build up some minor strain due to its substitution for Cd. Despite the stacking faults, however, the epitaxy is still conserved. Careful inspection of Fig. 2b and 2c suggests that there is a Cu deficient layer indicated by the oval where there is an apparent decrease in the Cu signal between the Cu rich layer and the CIGS that is filled by excess Cd (see 2b.) and Se signals (see 2c.). This indicates the possible formation of a buried *p-n* homojunction as in the case of CBD-CdS/CIGS[7, 8].

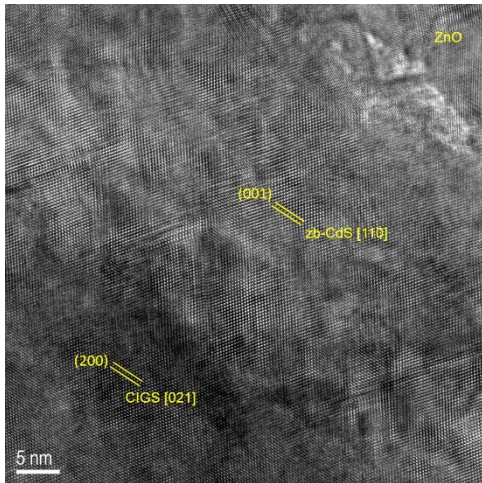


Fig. 1 High resolution TEM image showing zb CdS on CIGS with the epitaxial relationship indicated.

Another typical STEM-EDS map from these regions is shown in Fig. 3. Interestingly, we find some local domains in

the CdS where Cd is completely depleted and replaced by Cu as indicated by the circled region in Fig. 3a. Quantitative EDS analysis reveals its composition: Cu 65.8%, Cd 0.6%, S 33.6%, which is very close to  $\text{Cu}_2\text{S}$ . Fig. 4 is a HREM image of the highly Cd-depleted region. The yellow square box corresponds to the circled region in the Cd map in Fig. 4a. From the fast Fourier transform (FFT) of the image in the boxed region (see inset) the structure can be determined and is described well by

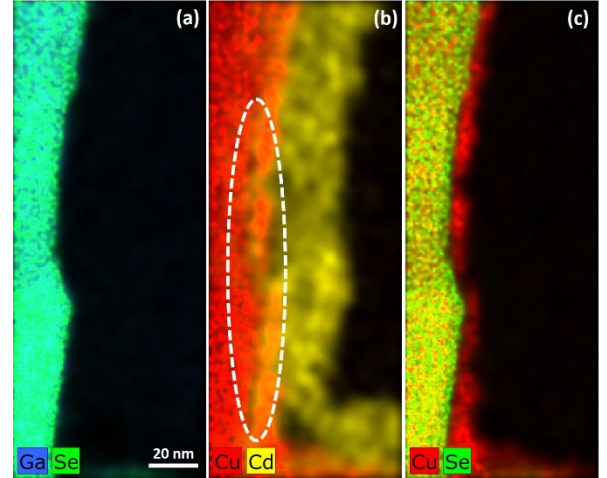


Fig. 2 STEM-EDS maps obtained from the region shown in Fig. 1. Note the uniform Cu rich layer in CdS. The dotted white oval suggests the Cu deficient layer.

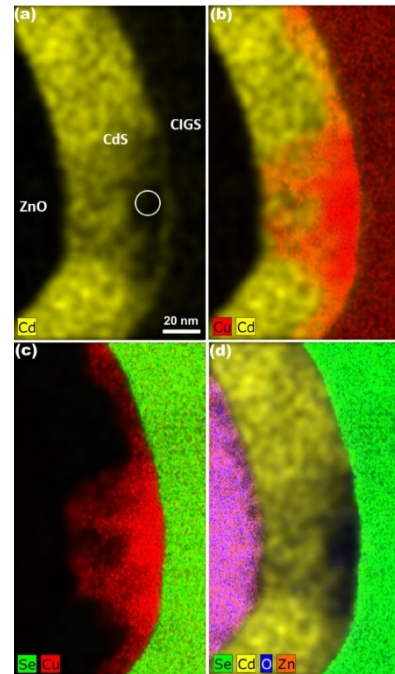


Fig. 3 STEM-EDS maps showing completely depleted Cd region (indicated by the circle in Fig. 3a) filled by high concentration Cu. EDS quantification indicates  $\text{Cu}_2\text{S}$  in the circled region. Note the Cu distribution through the entire CdS layer (Fig. 3c).

cubic  $\text{Cu}_2\text{S}$  with lattice parameter  $a = 0.561$  nm, consistent with the  $\text{Cu}_2\text{S}$  powder diffraction file card number 00-053-0522. Thus, in some cases the heterojunction partner material in some portions of the heterojunction is  $\text{Cu}_2\text{S}$ , epitaxially grown on the CIGS with the same orientationship as we reported for cubic CdS on CIGS[2].  $\text{Cu}_2\text{S}$  is a known p-type semiconductor with a band gap of about 1.15 eV and was widely studied for CdS- $\text{Cu}_2\text{S}$  solar cells [9, 10]. It has a comparable band gap to CIGS and can potentially form its own collecting heterojunction with the CdS surrounding it. As with CdS,  $\text{Cu}_2\text{S}$  contains a large number of defects and thus is not expected to yield photocurrent from the  $\text{Cu}_2\text{S}$  itself, as observed.

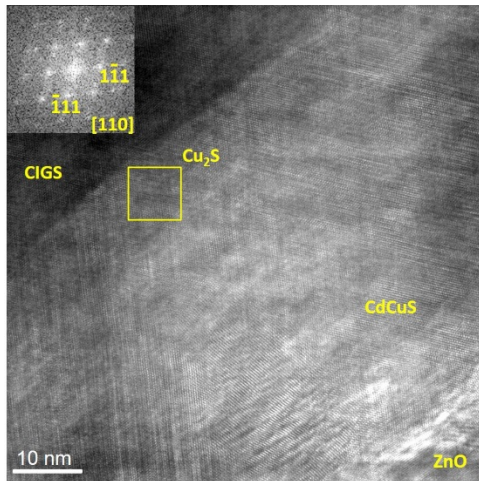


Fig. 4 HREM image of highly Cd depleted region. The region indicated by the yellow square box, which can be well indexed according to cubic  $\text{Cu}_2\text{S}$  from FFT inset, corresponds to the circled region in Fig. 3a.

#### IV. CONCLUSIONS

A STEM-EDS mapping technique was utilized to study the elemental intermixing across the PVD-CdS/CIGS heterojunction with special emphasis on Cu and Cd elements. Uniform Cu rich domains are found in the CdS and have no pronounced effect on epitaxy but appear to induce some stacking faults. Pure copper sulfide  $\text{Cu}_2\text{S}$  is also confirmed in some local regions in CdS matrix. While the open circuit voltage of the device is reduced somewhat the resulting heterojunctions still yield high current and fill factor.

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